

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



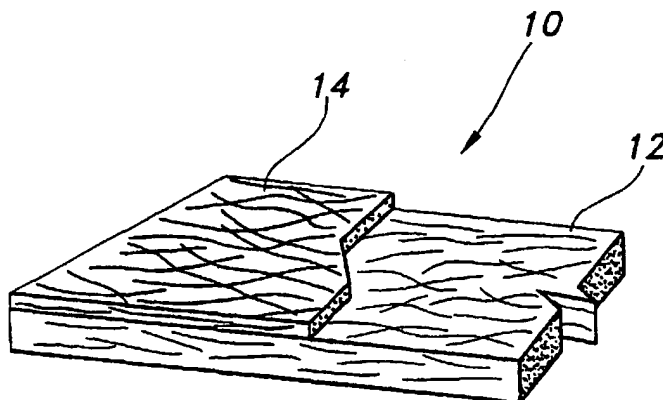
(43) International Publication Date
4 January 2001 (04.01.2001)

PCT

(10) International Publication Number
WO 01/00917 A1

- (51) International Patent Classification⁷: **D04H 13/00,**
D01F 6/46, B32B 5/26
- (21) International Application Number: PCT/US00/18000
- (22) International Filing Date: 29 June 2000 (29.06.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/141,429 29 June 1999 (29.06.1999) US
09/607,067 29 June 2000 (29.06.2000) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DURABLE MULTILAYER NONWOVEN MATERIALS



(57) Abstract: A durable multi-layered meltblown fiber web is provided having a first layer of fine crystalline polypropylene fibers and a second layer of fibers bonded directly to the first layer of fibers. The second layer of fibers is formed from a blend of a crystalline polyolefin and an amorphous polyalphaolefin and can be of a similar size or larger average size than the fibers of the first layer. The multilayer meltblown fiber webs are durable, having a reciprocating abrasion resistance in excess of 1000 cycles, and can also provide a highly pliable web having improved drape.

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DURABLE MULTILAYER NONWOVEN MATERIALS**BACKGROUND OF THE INVENTION**

Nonwoven fabrics have been used as or in sorbents, wipers, filters, protective fabrics as well as numerous other end-use applications. With regard to sorbents and/or wipers, meltblown fiber webs have been used as pre-moistened or saturated wipes such as described in U.S. Patent No. 4,775,582 to Win et al. Similarly, abrasive or dual-textured meltblown fiber webs have been used as industrial and household wipers such as described in U.S. Patent No. 4,833,003 to Win et al. Meltblown fiber webs provide a porous fine fiber structure having numerous small interstitial spaces throughout the web. Thus, polyolefin meltblown fiber webs have excellent absorbency and wicking characteristics for oil and, if treated, for aqueous and other liquids. As further specific examples, meltblown fiber webs have been used, either alone or in combination with other materials, in various other applications requiring good absorbency such as, for example, absorbent floor mats, oil booms and so forth.

However, many industrial or "heavy-duty" applications of such sorbents and wipes expose the nonwoven web to significant compressive and/or abrasive forces. These and other forces acting on the sorbent can often result in peeling or fraying of the fabric. As but one example, nonwoven sorbents are often utilized as floor mats in working areas to absorb oil, grease or other like substances that are spilled on the floor in the course of work. By absorbing the grease and/or oil spilled on the floor it becomes less slippery for workers and thereby provides a safer working environment. In this regard, many sorbents can begin to fray, develop pilling, delaminate or otherwise deteriorate upon exposure to such rigorous treatment. When a fabric begins to pull apart or degrade, the fabric can experience a significant loss in its ability to absorb liquids. Additionally, degradation of a fabric due to rigorous treatment is also undesirable from the standpoint of generating lint or particle fall-out. Still further, fabric degradation can also be undesirable when used as a floor mat since the separation of layers, fraying or other degradation can create an irregular surface.

Nonwoven webs having an outer layer of thick fibers that alter or otherwise improve fabric properties are known. As an example, a wipe, which is sufficiently abrasive to serve as a scrubbing wipe without using added abrasive materials is described in U.S. Patent No. 4,659,609 to Lamers et al. Lamers discloses a layered abrasive web including a supporting layer and a meltblown abrasive layer intimately bonded together. The

meltblown abrasive layer generally has a basis weight of from about 5 to about 25 grams per square meter (g/m^2) and is formed from fibers having an average fiber diameter of about 40 micrometers or more. As a further example, U.S. Patent No. 5,429,854 to Currie et al. describes an absorbent composite material that includes an apertured and shot-laden meltblown fiber web and nonwoven supporting layer. In addition, U.S. Patent No. 5,639,541 to Adam describes an oil sorbent having improved abrasion resistance and, in one aspect, Adam describes a fine meltblown fiber web having a layer of coarse fibers bonded thereto. The coarse fibers have a fiber size larger than that of the fine meltblown fibers and provide increased abrasion resistance to the fabric. While providing a highly absorbent material with good abrasion resistance, many applications and uses require still greater abrasion resistance and durability.

In addition to durability, in many wiping or cleaning operations it is often desirable that the fabrics also have improved cloth-like drape and/or a non-abrading surface. This is particularly desirable in many wipes used for cleaning or applying active agents to the skin or other sensitive surfaces. Abrasiveness of the fabric, and thus the amount of skin irritation resulting from use of the wipe, can often be increased by the presence of lint, shot or other irregularities in the web as well as the stiffness or hardness of the fabric itself.

The durability of nonwoven fabrics can often be improved by increasing inter-fiber bonding such as by the addition of external adhesives or by thermally point bonding the nonwoven fabric. However, the improved abrasion resistance would come at the expense of the overall absorbency and drape of the fabric. Thus, the ability to achieve improved durability without sacrificing other desired attributes of the nonwoven fabric has proven difficult.

25

SUMMARY OF THE INVENTION

The aforesaid needs are fulfilled and the problems experienced by those skilled in the art overcome by the nonwoven fabrics of the present invention comprising a first layer of meltblown fibers and a second layer of meltblown fibers wherein the second layer of fibers comprise a blend of from 0% to about 95% by weight of a crystalline olefin polymer and from 100% to about 5% by weight of an amorphous olefin polymer. In addition, the second layer of fibers is autogenously bonded to the first layer of fibers. Further, the multi-layered nonwoven web can have an abrasion resistance in excess of 250 cycles. Desirably, the amorphous polyolefin comprises between about 5% and about 50% of the fibers of the second layer. The amorphous polyolefin polymer can comprise polymers

having a crystallinity below 20% and, as examples, can comprise one or more propylene homopolymers, ethylene-propylene copolymers, propylene-butene copolymers and/or other propylene-alphaolefin copolymers. In one aspect, the amorphous polyolefin polymer comprises a polyolefin elastomer. In a further aspect, the first layer of fine fibers desirably
5 can have an average fiber diameter less than about 8 micrometers and the second layer of fibers can comprise fibers having a substantially similar average diameter or, in the alternative, fibers of a larger average fiber diameter. The basis weight ratio of the first layer to the second layer can be about 1:1 or, in a further aspect, can be about 2:1 or more. Additionally, the fibers of the first layer desirably comprise a propylene polymer
10 such as, for example, crystalline polypropylene. Further, the fibers of the second layer desirably comprise a blend of a crystalline propylene polymer and an amorphous propylene polymer.

In a further aspect of the invention, a durable multilayer nonwoven web composite material is provided having a first layer of meltblown fibers and a second outermost layer
15 of meltblown fibers autogenously bonded to the first layer and wherein the multilayer nonwoven composite material includes a tertiary material, such as particulate materials and/or short fibrous matter, dispersed within at least one of said first and second layers. As examples, the tertiary material can comprise pulp and/or cellulosic fibers and are desirably dispersed throughout each of the layers of the multilayer nonwoven composite
20 material. The fibers of the second layer desirably comprise from 5% to 95% of an amorphous polyolefin and from 5% to 95% of a crystalline polyolefin. The fibers of the first layer desirably comprise a propylene polymer such as, for example, crystalline polypropylene. Further, the fibers of the second layer desirably comprise a blend of crystalline polypropylene and an amorphous propylene polymer. In a particular
25 embodiment, the amorphous polyolefin desirably comprises a propylene elastomer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a partially broken-away elevated view of a section of a multilayer
30 meltblown fiber web of the present invention.

Figure 2 is a schematic diagram of an exemplary apparatus for forming multilayer meltblown fiber webs of the present invention.

Figure 3 is a cross-sectional side view of a section of a multilayer meltblown fiber web of the present invention.

35 Figure 4 is a schematic diagram of an exemplary apparatus for forming a multilayer meltblown fiber composite structure of the present invention.

DEFINITIONS

As used herein, the term "comprising" is inclusive or open-ended and does not exclude additional unrecited elements, compositional components, or method steps.

5 As used herein the term "nonwoven" fabric or web means a web having a structure of individual fibers or threads which are interlaid, but not in an identifiable manner as in a knitted or woven fabric. Nonwoven fabrics or webs have been formed by many processes such as for example, meltblowing processes, spunbonding processes, hydroentangling, air-laying, carded web processes, and so forth.

10 As used herein the term "polymer" generally includes but is not limited to, homopolymers, copolymers, such as for example, block, graft, random and alternating copolymers, terpolymers, etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" includes all possible spatial configurations of the molecule. These configurations include, but are not limited to isotactic, syndiotactic
15 and random symmetries.

As used herein, the term "machine direction" or MD means the direction in which it is produced. The term "cross machine direction" or CD means the direction generally perpendicular to the MD.

As used herein, the term "liquid" refers to liquids generally regardless of form and
20 includes solutions, emulsions, suspensions and so forth.

As used herein, the term "autogenous bonding" refers to inter-fiber bonding between discrete parts and/or surfaces independently of mechanical fasteners or external additives such as latex adhesives, solders and the like.

25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

In reference to FIG. 1, nonwoven web 10 comprises at least two layers including a first layer 12 of meltblown fibers and a second layer 14 of meltblown fibers. The first layer is desirably a relatively thick layer having numerous interstitial spaces throughout the web.
30 When in use, the second layer 14 of nonwoven web 10 desirably faces the abrading or compacting force. For example, second layer 14 of nonwoven web 10 desirably faces up when used as a floor mat or faces the surface to be acted upon when used as a wiper or a cleaning implement. The nonwoven web is typically made in the form of a sheet and stored in roll form. The sheet material can then be cut to the desired dimensions and/or
35 shape as needed. Sorbents and wipes are commonly cut into square or rectangular sections. By way of example only, floor mats are often cut into segments having

dimensions of approximately 45 cm x 45 cm or more. In addition, wipes are commonly cut into segments having dimensions of approximately 12 cm x 12 cm or more. The materials can be converted as desired and specifically tailored to meet the needs of the end user. As particular examples, the materials can be readily converted into floor mats such as those described in U.S. Patent No. 4,609,580 to Rockett et al. or into pre-moistened hand-held wipers such as described in U.S. patent 4,778,048 to Kaspar et al.; the entire contents of the aforesaid references are incorporated herein by reference.

The multilayer nonwoven web, when evaluating the exposed second layer, desirably has a reciprocating abrasion resistance of at least 500 cycles and more desirably has a reciprocating abrasion resistance in excess of about 1000 and still more desirably has a reciprocating abrasion resistance in excess of about 1500 cycles. Moreover, the present invention provides a meltblown fiber nonwoven web that exhibits excellent abrasion resistance without significantly degrading the strength and/or absorbency of the same. Thus, when utilized as a sorbent material or liquid delivery material, the nonwoven webs of the present invention can have an absorbent capacity for oil of at least about 8 grams and desirably have an absorbent capacity of about 11 grams or more and still more desirably have an absorbent capacity of about 15 grams or more. In addition, the sorbent material can have a specific capacity of at least about 8 grams oil per gram substrate and more desirably has a specific capacity of at least about 10 grams oil per gram substrate and still more desirably has a specific capacity of at least about 12 grams oil per gram substrate. In addition, the sorbent material also has the ability to retain absorbed fluid. Still further, the sorbent material is re-usable. In this regard the sorbent material can be dried, such as with compressive force (e.g. wrung-dry) without disintegrating or substantially degrading the same.

In a further aspect, when utilized as a wiper, the nonwoven web can provide a durable material that also provides a more pliable sheet and/or a less abrading surface, i.e. a surface that is softer or smoother on the skin, compared to like fabrics. Moreover, the improved drape and/or compliance of the multilayer nonwoven web can be provided while substantially maintaining the strength and integrity of the multilayer meltblown material.

First layer 12 desirably comprises a nonwoven web of fine fibers having an average fiber diameter of less than about 7 micrometers and more desirably having an average fiber diameter between about 1 micrometer and about 6 micrometers. The first layer desirably has a basis weight of at least about 20 grams/square meter (g/m^2) and more desirably has a basis weight between about 50 g/m^2 and about 500 g/m^2 . As examples, sorbent materials can employ a first layer having a basis weight between about 150 g/m^2

and about 400 g/m² and wipes employ a first layer having a basis weight between about 30 and 80 g/m². The first layer of fibers can be made by various methods known in the art and desirably comprises a nonwoven web of meltblown fibers. Meltblown fibers are generally formed by extruding a molten thermoplastic material through a plurality of die capillaries as molten threads or filaments into converging high velocity, usually hot, gas (e.g. air) streams which attenuate the filaments of molten thermoplastic material to reduce their diameter. Thereafter, the meltblown fibers can be carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. Meltblown processes are disclosed, for example, in U.S. Patent No. 3,849,241 to Butin et al.; U.S. Patent No. 4,100,324 to Anderson et al., U.S. Patent No. 3,959,421 to Weber et al.; U.S. Patent No. 5,652,048 to Haynes et al.; and U.S. Patent No. 5,271,883 to Timmons et al. Meltblown fiber webs having high bulk, such as those described in U.S. Patent No. 5,652,048 to Haynes et al. are particularly well suited for use with the present invention. The entire content of U.S. Patent No. 5,652,048 to Haynes et al. is incorporated herein by reference. The first layer of fine fibers can be formed by a single meltblown die or by consecutive banks of meltblown fiber dies by depositing the fibers on a moving forming surface. In this regard, as used herein and throughout the term "layer", unless otherwise noted, is used broadly and can comprise one or more sub-layers of like polymeric material.

Suitable thermoplastic polymers for forming the first layer of fine fibers include, but are not limited to, polyolefins (e.g., polypropylene and polyethylene), polycondensates (e.g., polyamides, polyesters, polycarbonates, and polyarylates), vinyl polymers, polyols, polydienes, polyurethanes, polyethers, polyacrylates, polycarbonates, polystyrenes, and so forth. Examples of suitable polyolefins include, by way of example only, polyethylene, polypropylene, polybutene and copolymers and/or blends thereof. As examples, the fibers can comprise propylene and/or ethylene polymers and copolymers thereof and more particularly can comprise copolymers of ethylene and/or propylene with alpha-olefins. Additional examples of polymers suitable for making fine fibers also include poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), nylon, polybutylene, polyethylene terephthalate, polybutylene terephthalate, and so forth. Additionally, thermoplastic elastomers are also suitable for use with the present invention such as, for example, ethylene-propylene rubbers, styrenic block copolymers, copolyester elastomers, polyamide elastomers and so forth. In a particular embodiment, the first layer of the nonwoven web comprises fibers of crystalline polymers having a crystallinity greater than 20% and still more desirably a crystallinity of about 30% or more and even still more desirably a crystallinity of about 50% or more. In an exemplary embodiment, the fine fiber web can comprise an inelastic crystalline propylene polymer.

The fibers of the second layer can comprise between 5% and 100% amorphous polyolefin. Desirably, however, the fibers comprise a composite or blend of two or more olefin polymers. The second layer comprises thermoplastic fibers comprising an amorphous polyolefin and/or a blend of an amorphous polyolefin polymer with a second polyolefin. As used herein, "amorphous" polyolefins include those having a crystallinity less than 20%. Desirably, the amorphous polyolefins have a crystallinity less than about 10% and still more desirably a crystallinity below about 7%. The amorphous polymer is desirably blended with one or more different polyolefins such as those described herein above and, desirably, comprises an ethylene polymer (e.g. liner low-density polyethylene and/or high-density polyethylene) or a crystalline propylene polymer. The amorphous polyolefin desirably comprises between about 5% and about 95% of the polymeric component of the fiber and more desirably comprises between about 10% and about 50% of the polymeric component of the fiber. In a further aspect, when the second layer comprises larger fibers the amorphous polyolefin desirably comprises between about 5% and about 45% and even more desirably comprises between about 10% and 35% of the polymeric component of the fiber. However, with regard to personal care wipers and many absorbent composite fabrics, the amorphous polyolefin desirably comprises between about 10% and about 95% by weight of the fiber and even more desirably comprises between about 10% and 50% by weight of the polymeric component of the fiber.

Exemplary amorphous polyolefins include amorphous polyalphaolefins that can comprise, by way of example only, one or more propylene homopolymers, ethylene-propylene copolymers, propylene-butene copolymers, and copolymers of propylene with other alphaolefins. Exemplary commercially available amorphous polyalphaolefins include, by way of example only, the REXTAC family of amorphous polyalphaolefins from Huntsman Corp. and VESTOPLAST polymers from Creanova AKG. A particularly preferred copolymer comprises a copolymer of propylene and 1-butene under the trade designation REXTAC 2730. In a further aspect, the amorphous polyolefin can comprise an elastomer. In this regard, amorphous olefin elastomers believed suitable for use with the present invention include those available from Huntsman Corporation under the trade name REXFLEX FLEXIBLE POLYOLEFINS. Further, additional amorphous polyolefins believed suitable for use in the present invention include stereoblock polymers. The term "stereoblock polymer" refers to polymeric materials with controlled regional tacticity or stereosequencing to achieve desired polymer crystallinity. By controlling the stereoregularity during polymerization, it is possible to achieve atactic-isotactic stereo blocks. Methods of forming polyolefin stereoblock polymers are known in the art and are described in the following articles: G. Coates and R. Waymouth, "Oscillating Stereocontrol:

A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene" 267 Science 217-219 (January 1995); K. Wagener, "Oscillating Catalysts: A New Twist for Plastics" 267 Science 191 (January 1995). Stereoblock polymers and methods of their production are also described in U.S. Patent No. 5,549,080 to Waymouth et al. and U.S. Patent No.

- 5 5,208,304 to Waymouth. et al. Additional amorphous polyolefins believed suitable for use with the present invention are described in European Patent No. 0475307B1, European Patent No. 0475306A1, U.S. Patent No. 3,954,697, U.S. Patent 3,679,775 and U.S. Patent No. 4,143,858.

10 The second layer of the nonwoven web can comprise fibers having an average size or denier substantially similar to that of the fibers comprising the first layer. Alternatively, the second layer of the nonwoven web can comprise fibers having a significant number of larger fibers. As an example, the first layer can have an average fiber size less than about 7 micrometers and the second layer can have an average fiber size in excess of about 15 micrometers. As further examples, the fibers of the second layer can have an average
15 fiber diameter between about 10 and about 35 micrometers and still more desirably an average fiber diameter of between about 12 micrometers and about 25 micrometers. In one aspect of the invention, the second layer can comprise fibers having an average fiber size at least about 10 micrometers larger than that of the first layer. Further, the second layer desirably comprises a significant number of fibers in excess of about 20 microns and
20 further can have a substantial number of fibers in excess of about 35 microns. In this regard the second layer can comprise a relatively homogeneous collection of larger fibers or a mixture or blend of fibers of varying shape and/or thickness. Further, larger fibers can be created wherein smaller individual fibers "rope" or otherwise become length-wise bonded so as to collectively form larger fibers.

25 The second layer of meltblown fibers can have a basis weight similar to that of the first layer. However, the basis weight of the first layer is desirably greater than that of the second layer. The basis weight ratio of the first layer to the second layer is desirably about 2:1 or more and as an example can be between about 4:1 to about 15:1. In a further aspect, the second layer desirably has a basis weight of at least about 17 g/m² and more desirably has
30 a basis weight between about 20 g/m² and about 68 g/m², and still more desirably between about 34 g/m² and about 58 g/m².

The second layer of fibers can also be made by meltblown processes and, desirably, the fibers are deposited directly onto the first layer of the nonwoven web in a semi-molten state such that the fibers autogenously bond to the first layer. When making
35 meltblown fibers of larger diameter, conventional meltblowing equipment can also be used to produce such fibers by properly balancing the polymer throughput, diameter of the die

tip orifice, formation height (i.e. the distance from the die tip to the forming surface), melt temperature and/or draw air pressure. As a specific example, and in reference to the meltblown apparatus 20 depicted in FIG. 2, a first series of meltblown banks 22, 23 produce a substantially homogeneous first layer 24 upon forming wire 26 and the process conditions or equipment comprising last meltblown bank 28 in the series of meltblown banks is adjusted such that it deposits a second layer 30 of larger fibers over the newly formed first layer of meltblown fibers 24, and thereby forming multilayer nonwoven 32. With regard to making larger polypropylene fibers, larger fibers can be achieved on conventional meltblowing assets by reducing the primary air temperature and pressure as well as lowering the formation height. The thickness or basis weight of the second layer can be increased as desired by increasing the number of consecutive meltblown banks altered to provide such fibers. It is noted that alteration of other parameters alone or in combination with the aforesaid parameters may also be used to achieve large fibers and/or thicker webs. Methods of making larger meltblown fibers are described in more detail in U.S. Patent No. 5,639,541 to Adam and U.S. Patent No. 4,659,609 to Lamers et al.; the entire contents of each of the aforesaid references are incorporated herein by reference. In a further aspect, it is possible to deposit more than one large fiber layer on the first fine fiber layer.

After the deposition, the multiple layers can, optionally, be further bonded together. If, however, further bonding is desired it is preferred to employ a bond pattern that does not bond more than about 15% of the surface area of the sheet. Desirably the bonded regions of the nonwoven fabric comprise between 0.5% and about 10% of the surface area of the fabric and still more desirably comprises between about 1% and about 5% of the surface area of the fabric. Utilizing higher bonding areas can significantly reduce the absorbent capacity and/or significantly degrade the strength and/or drape of the nonwoven fabrics. The multilayer laminate can be bonded by continuous or substantially continuous seams and/or discontinuous bonded regions. Preferably the multi-layered sorbent materials are point bonded. As used herein "point bonded" or "point bonding" refers to bonding one or more layers of fabric at numerous small, discrete bond points. For example, thermal point bonding generally involves passing one or more layers to be bonded between heated rolls such as, for example, an engraved patterned roll and an anvil roll. The engraved roll is patterned in some way so that the entire fabric is not bonded over its entire surface, and the anvil roll is usually flat. Numerous bond patterns have been developed in order to achieve various functional and/or aesthetic attributes, the particular nature of the pattern is not believed critical to the present invention. Exemplary bond patterns are described in U.S. Patent 3,855,046 to Hansen et al., U.S. Design Patent No. 356,688 to

Uitenbroek et al. and U.S. Patent No. 5,620,779 to Levy et al. These and other bond patterns can be modified as necessary to achieve the desired bonding frequency and area.

In a further aspect and in reference to FIG. 3, a multilayer nonwoven sheet 40 is provided having a third layer 46 similar or identical in composition to the second layer 44 and that is attached to the opposing side of first layer 42 and thus the first layer 42 of fine fibers is positioned between the second and third layers 44, 46. The third layer desirably comprises fibers having a fiber size substantially similar to either those forming the first or second layer. In a particular embodiment, a highly pliable sorbent and/or wipe is provided having improved durability wherein the fibers of each of the first, second and third layers have an average fiber diameter less than about 7 micrometers and, still more desirably, have an average fiber size less than about 5 micrometers. The nonwoven webs can be made using conventional meltblowing equipment such that, when using a multiple bank system, at least the first and last banks extrude the amorphous polyolefin blends described herein above. In an alternate embodiment of the invention, the second and third layers can comprise a meltblown fiber web having an average fiber size greater than that of the first layer. In an exemplary embodiment, the first layer of fine fibers can comprise an inelastic propylene polymer having a crystallinity greater than 50% and the second and third layers of larger fibers can comprise a blend of an amorphous propylene polymer and an inelastic propylene polymer having a crystallinity greater than about 50%.

In still a further aspect of the invention, when the second layer comprises fibers having a significantly larger diameter than those of the first layer, a third layer can be included within the multilayer laminate wherein the third layer of fine fibers is positioned adjacent the first layer of fine fibers and the second layer of larger fibers and further wherein the meltblown fibers of the third layer comprise a polymer composition similar and/or identical to that comprising the second layer. In this regard, when forming a multilayer nonwoven web from a series of meltblown banks, the second to last bank can utilize the same polymer composition as the meltblown bank for forming the second layer wherein the process conditions and/or equipment is adjusted so as to form fine fibers similar to those of the first layer.

Additionally, one or more of the layers comprising the multilayer nonwoven web can optionally include fibrous or particulate matter within the nonwoven web. In this regard, meltblown fiber web composites can be made incorporating fibrous or particulate materials therein by one or more processes known in the art. As an example, meltblown fiber composites can be formed utilizing one or more "coforming" processes. Suitable coforming processes are described, by way of example only, in commonly assigned U.S. Patent 4,818,464 to Lau; U.S. Patent 4,100,324 to Anderson et al.; U.S. Patent 5,284,703 to

Everhart et al.; and U.S. Patent 5,350,624 to Georger et al.; the entire contents of the aforesaid references are incorporated herein by reference. Generally speaking, coform materials can be made by a process in which one or more meltblown die heads are arranged near a chute through which other materials are added to the web while it is forming. Such other materials may be, for example, pulp, superabsorbent particles, cellulose and/or staple fibers. Meltblown fiber webs incorporating such materials desirably contain between about 30% and about 85% by weight of the fibrous or particulate material and still more desirably contain between about 50% and about 75% by weight of the fibrous or particulate material. In many absorbent products, pulp and/or cellulosic fibers are particularly desirable due to their availability and low cost. As a particular example of an absorbent material of the present invention, a multilayer nonwoven web can be provided comprising a first layer of crystalline propylene polymer fibers and a second layer of fibers comprising a blend of an amorphous propylene polymer and a crystalline propylene polymer wherein both layers contain pulp and/or cellulosic fibers dispersed therein.

In reference to FIG. 4, apparatus 50 can be used to make an exemplary absorbent and highly pliable multilayer nonwoven web of the present invention. Picker-roll assembly 52 can be used to generate a stream of short fibers 54, e.g. pulp, between converging first and second streams of thermoplastic meltblown fibers 57, 59. The first bank of meltblown dies 56 forms the first stream of meltblown fibers 57 and the second bank of meltblown dies 58 forms the second stream of meltblown fibers 59. First and second polymer compositions, as described herein above, can be fed into the first and second meltblown dies 56, 58 respectively. The stream of short fibers 54 is captured within the converging streams of thermoplastic polymer fibers thereby forming an autogenously bonded multilayer meltblown fiber composite material 62 upon forming surface 60. The apparatus and processes for forming such composite structures are more thoroughly described in U.S. Patent 5,350,624 to Georger et al. In an exemplary embodiment, a composite nonwoven material is provided comprising between about 60 to 70% pulp and wherein the first layer comprises a crystalline propylene polymer and the second layer comprises between about 50% and 90% of a crystalline propylene polymer and between about 10% and 50% of an amorphous propylene polymer.

The multilayer nonwoven materials of the present invention can be used alone or as part of a laminate structure in combination with additional materials. In addition, the multilayer fabric of the present invention can, optionally, include various additives or topically applied chemicals in order to impart additional or improved characteristics to the nonwoven fabric. Such additives and/or treatments are known in the art and include, for example, alcohol repellence treatments, anti-static treatments, wetting chemistries (i.e.

compositions that make a surface more hydrophilic), fire retardants, disinfectants, anti-bacterial agents, anti-fungal, germicides, virucides, detergents, cleaners and so forth. Examples of suitable additives and/or topical treatments suitable for use with the present invention include, but are not limited to, those described in U.S. Patent Nos. 3,973,068
5 and 4,070,218 to Weber et al., U.S. Patent No. 4,587,154 to Hotchkiss et al., U.S. Patent No. 4,328,279 to Meitner et al., U.S. Patent No. 5,696,191 to Nohr et al. and U.S. Patent No. 5,770,549 to Gross. In addition, the multi-layered material may be treated with the compositions described in commonly assigned U.S. Patent Application Nos. 09/320324 filed May 36, 1998 and 09/293294 filed April 16, 1999 to Yahiaoui et al., the entire
10 contents of the aforesaid references are incorporated herein by reference.

Addition of chemical treatments to the materials of the present invention can be accomplished by various methods known to those skilled in the art. Preferred methods substantially uniformly apply the wetting chemistry throughout the substrate. As examples, the chemical treatments can be topically applied during or post web formation and/or
15 added internally prior to extrusion. When added internally, a subsequent "blooming" step may be needed in order to bring the chemistry to the surface of the fiber. A method for topically treating the porous material includes passing the sorbent sheet or fabric under an applicator, such as a spray boom, wherein an aqueous liquid, containing the desired chemistry, is applied or sprayed onto the porous substrate. A vacuum can, optionally, be
20 positioned under porous substrate in order to help draw aqueous liquid through the web and improve the uniformity of treatment. Thereafter the porous substrate, with the aqueous liquid thereon, is dried. Upon driving off the water, the desired chemistry remains upon or in the substrate. As a further example, spray booms can be located adjacent each bank or series of meltblown dies in order to spray the blown fibers with the desired
25 chemistry prior to formation of the meltblown web on the forming wire. The heat of the blown fibers causes water or other solvents to flash off. Additional methods of treating substrates are also suitable for use with the present invention such as, for example, "dip and squeeze" processes, brush coating processes and so forth. The wetting agent or other chemical composition generally comprise from about 0.1 % to about 10% of the total
30 weight of the dried nonwoven web. However, the add-on weight of a particular chemistry can vary outside these ranges depending on the particular purpose and function of the same.

The multilayer nonwoven webs of the present invention can be used in a variety of materials and applications. As but a few examples, the multilayer nonwoven webs of the
35 present invention are well suited for use as wet and/or dry wipes (including personal, medical, industrial, and/or residential uses), absorbent materials and sorbents, liquid

delivery products, protective fabrics and so forth. As a particular example, the multilayer nonwoven webs can be utilized in an absorbent floor mat. As a further example, the multilayer nonwoven webs can be utilized as a pre-moistened personal care wipe.

5

TESTS

Absorption Capacity: a 4-inch by 4-inch specimen is initially weighed. The weighed specimen is then soaked in a pan of test fluid (e.g. paraffin oil) for three minutes. The test fluid should be at least 2 inches (5.08 cm) deep in the pan. The specimen is removed
10 from the test fluid and allowed to drain while hanging in a "diamond" shaped position (i.e. with one corner at the lowest point). The specimen is allowed to drain for 5 minutes. After the allotted drain time the specimen is placed in a weighing dish and then weighed.
Absorption Capacity (g) = wet weight (g) - dry weight (g); and Specific Capacity (g/g) =
Absorption Capacity (g)/dry weight (g).

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Reciprocal Abrasion Test: The "reciprocating abrasion test" (RAT) involves stroking a sample, usually 5.5 inch by 7 inch (140 mm by 180 mm) of fabric with a silicone rubber abrasive and then evaluating the fabric for pilling, roping and fuzzing. The horizontally reciprocating dual head abrasion tester used herein is the Model no. 8675 from United
20 States Testing Company, Inc. of Hoboken NJ. The abrasant, silicone solid rubber fiber glass reinforced material has a rubber surface hardness of 81A Durometer, a Shore A of 81 (± 9) and is 36 inches (914 mm) by 4 inches (102 mm) by 0.005 inches (0.127 mm) thick and is available as catalogue no. 4050 from Flight Insulations Inc., (distributors for Connecticut Hard Rubber) of Marietta, Ga. The abrasant should be conditioned by
25 cycling it over a scrap piece of the material to be tested about 200 times. The test sample should be free of folds, creases etc., mounted in the instrument on cork backing with the outermost second fiber layer facing up and cleaned of residual surface fibers with a camel hair brush. The abrasant arm should be lowered and the cycling begun at a total weight of 1180 g with half of the weight on each of the two abrasant arms. The cycling of the
30 abrasant over the specimen is repeated until formation of extensive fiber piling and surface destruction.

Peel Test: In peel or delamination testing a laminate is tested for the amount of tensile force which will pull the layers of the laminate apart. Values for peel strength are obtained
35 using a specified width of fabric, usually 4 inches (102 mm), clamp width and a constant rate of extension. The sample is delaminated by hand a sufficient amount to allow it to be

clamped into position. The specimen is clamped in, for example, an Instron Model TM, available from the Instron Corporation, 2500 Washington St., Canton, MA 02021, or a Thwing-Albert Model INTELLECT II available from the Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, PA 19154, which have 3 inch (76 mm) long parallel clamps. The sample specimen is then pulled apart at 180° of separation and the tensile strength recorded.

Crystallinity: Crystallinity can be determined is through the use of wide-angle X-ray diffraction (WAXD). The percent crystallinity may be calculated with the following equation:

$$\text{percent } C = (A_c / (A_a + A_c)) \times 100$$

in which percent C again represents percent crystallinity, A_c represents the total area under the crystalline peaks of the WAXD pattern and $A_a + A_c$ represents the total area under the WAM pattern, A_a representing the amorphous peaks.

Cup Crush: The softness of a nonwoven fabric may be measured according to the "cup crush" test. The cup crush test evaluates fabric stiffness by measuring the peak load or "cup crush" required for a 4.5 cm diameter hemispherically shaped foot to crush a 25 cm by 25 cm piece of fabric shaped into an approximately 6.5 cm diameter by 6.5 cm tall inverted cup while the cup shaped fabric is surrounded by an approximately 6.5 cm diameter cylinder to maintain a uniform deformation of the cup shaped fabric. An average of 10 readings is used. The foot and the cup are aligned to avoid contact between the cup walls and the foot which could affect the readings. The peak load is measured while the foot is descending at a rate of 40.6 cm/minute and is measured in grams. The cup crush test also yields a value for the total energy required to crush a sample (the "cup crush energy") which is the energy from the start of the test to the peak load point, i.e. the area under the curve formed by the load in grams on one axis and the distance the foot travels in millimeters on the other. Cup crush energy is therefore reported in g-mm. Lower cup crush values indicate a softer or more pliable laminate. A suitable device for measuring cup crush is a Sintech Tensile Tester and 500g load cell using TESTWORKS Software all of which are available from Sintech, Inc. of Research Triangle Park, NC.

Tensile Strength: Tensile strength or peak load measures the maximum load (gram force) before the specimen ruptures. A 4 inch by 6 inch sample is placed in a 1 inch by 1 inch rubber coated clamp or jaws and a 1 inch by 2 inch rubber coated clamp or jaws (with the longer dimension being perpendicular to the load) so that the machine direction (i.e. the direction in which the fabric is made) is parallel with the load. The sample is

placed in the jaws such that there is a 3 inch gage length. The test can be performed with an 1130 Instron Tensile Tester (available from Instron Corporation of Canton, MA) and utilizes a cross-head speed of 12 inches/minute and a 10 pound load cell. The load at rupture is reported in grams.

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EXAMPLES

Example 1: An 88 g/m² meltblown fiber web was made comprising a first layer of 47 g/m² fine fiber meltblown and a second layer of 41 g/m² larger fiber meltblown. The fine fiber meltblown comprised a crystalline polypropylene, available from Himont USA, Inc. under the designation Polypropylene PF015, and had an average fiber size of approximately 6 micrometers. The larger fiber meltblown comprised a blend of 65% by weight crystalline polypropylene, available from Himont USA, Inc. under the designation Polypropylene PF015, and 35% by weight amorphous polyalphaolefin, available from Huntsman Corporation under the designation REXTAC 2730, and had an average fiber size of approximately 18 micrometers. The resulting meltblown web had an oil absorbency of approximately 8 grams, a specific capacity of 8.3 g/g, a peel strength of 93 g (0.206 lb.), and an abrasion resistance in excess of 1500 cycles (using reciprocal abrasion test). Thus, a sorbent material is provided having both excellent absorbency as well as strength and durability.

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Example 2: An 88 g/m² meltblown fiber web was made comprising a first layer of 47 g/m² fine fiber meltblown and second layer of 41 g/m² larger fiber meltblown. The fine fiber meltblown comprised a crystalline polypropylene, available from Himont USA, Inc. under the designation Polypropylene PF015, and had an average fiber size of approximately 6 micrometers. The larger fiber meltblown comprised a blend of 50% by weight crystalline polypropylene, available from Himont USA, Inc. under the designation Polypropylene PF015, and 50% by weight amorphous polyalphaolefin, available from Huntsman Corporation under the designation REXTAC 2730, and had an average fiber size of approximately 20 micrometers. The resulting meltblown web had an oil absorbency of approximately 8 grams, a specific capacity of approximately 8 g/g, a peel strength of 108g (0.239 lb.), and an abrasion resistance in excess of 1500 cycles (using reciprocal abrasion test). Thus, a sorbent material is provided having both excellent absorbency as well as strength and durability.

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Example 3: A 75 g/m² multilayer meltblown fiber web composite was formed using angled dual-bank meltblowing equipment and processes as described in US patent No. 5,350,624 to Georger et al. The first bank extruded thermoplastic polymer fibers comprising PF015 polypropylene available from Himont USA, Inc. and the second bank extruded thermoplastic polymer fibers comprising an amorphous propylene polymer, FPO WL 120 available from Huntsman Corporation. The meltblown fiber composite comprised approximately 65%, by weight, CF405 pulp fibers available from Weyerhaeuser Company. The multilayer meltblown fiber composite had a tensile strength of 1250 g in the MD and 1102 g in the CD. In addition, the multilayer meltblown composite had cup crush value of 2872 (dry) and 1118 (wet, i.e. 300 weight percent saturation). Further, the multilayer meltblown fiber composite produced lower transepidermal water loss (TEWL) on users over extended and repeated use, i.e. the resulting wipes cause less irritation of the skin and/or degradation of skin barrier function. Thus, a multilayer meltblown composite was formed having good strength and drape while also providing a wipe having less abrasive properties.

Example 4: A first meltblown fiber web was formed, in accord with US Patent No. 5,811,178 to Adam et al., comprising PFO15 polypropylene fibers and had a basis weight of 390 g/m². The first meltblown fiber web was thermally point bonded. A 34 g/m² second layer was formed directly upon the first meltblown fiber web and comprised 80%, by weight, PFO15 polypropylene and 20%, by weight, of an amorphous propylene elastomer, FPO WL 121. The second layer was formed using an 8 inch forming height, an extrusion temperature of 380°F and with primary air temperature of 380°F at 3 psi. The second layer had fibers having a larger diameter than those of the first layer. The multilayer nonwoven web was point bonded along seams using mechanical compacting pressure. The resulting multilayer laminate had excellent absorbency and abrasion resistance.

Example 5: A multilayer meltblown fiber fabric was formed in-line using a multiple bank meltblown system. A first meltblown fiber layer was formed, in accord with US Patent No. 5,811,178 to Adam et al., of PFO15 polypropylene fibers and had a basis weight of 348 g/m². The process conditions of the last bank was modified by reducing the forming height and cutting the primary air pressure by 50%, thereby providing a second layer of fibers having a larger average diameter relative to the first layer. The second layer was formed upon the first layer, had a basis weight of 42 g/m² and the fibers comprised 70%, by weight, PFO15 polypropylene and 30%, by weight, of an amorphous propylene elastomer,

FPO WL 121. The resulting multilayer laminate exhibited excellent abrasion resistance and durability and also had a bulk of 0.17 inches a specific absorbent capacity of 8.8 g/g.

While various patents and other reference materials have been incorporated herein by
5 reference, to the extent there is any inconsistency between incorporated material and that of
the written specification, the written specification shall control. In addition, while the
invention has been described in detail with respect to specific embodiments thereof, and
particularly by the examples described herein, it will be apparent to those skilled in the art
that various alterations, modifications and other changes may be made without departing
10 from the spirit and scope of the present invention. It is therefore intended that all such
modifications, alterations and other changes be encompassed by the claims.

What is claimed is:

1. A durable multilayer nonwoven web comprising:
 - a first layer of first meltblown fibers, said first fibers comprising thermoplastic polymer and having an average fiber size of less than about 8 micrometers;
 - a second layer of second meltblown fibers autogenously bonded to said first layer
- 5 and comprising an outermost layer of said multilayer nonwoven web, and further wherein the polymeric portion of said second fibers comprise from 5% to 100% of an amorphous polyolefin and from 0% to 95% of a crystalline polyolefin; and
 - wherein said multilayer nonwoven web has an abrasion resistance in excess of 250 cycles under the reciprocal abrasion test.
2. The multilayer nonwoven web of claim 1 wherein the first fibers comprise a propylene polymer.
3. The multilayer nonwoven web of claim 2 wherein the crystalline polyolefin of said second fibers comprises a crystalline propylene polymer.
4. The multilayer nonwoven web of claim 3 wherein said amorphous polyolefin of said second fibers comprises an amorphous propylene polymer.
5. The multilayer nonwoven web of claim 4 wherein said amorphous polyolefin polymer of said second layer is selected from the group consisting of propylene homopolymers, ethylene-propylene polymers, propylene-butene polymers and propylene-alphaolefin polymers.
6. The multilayer nonwoven web of claim 4 wherein said amorphous polyolefin polymer of said second fibers comprises about 10% to about 50%, by weight, of the polymeric portion of said fibers.
7. The multilayer nonwoven web of claim 6 wherein said amorphous polyolefin polymer of said second layer comprises a propylene polymer having less than about 10% crystallinity.

8. The multilayer nonwoven web of claim 6 wherein the basis weight ratio of the first layer to the second layer is greater than about 2:1 and wherein the multilayer nonwoven web has an abrasion resistance in excess of 1000 cycles.
9. The multilayer nonwoven web of claim 8 wherein the second layer has a basis weight less than about 68 g/m² and said first layer has a basis weight at least greater than or equal to the basis weight of the second layer.
10. The multilayer nonwoven web of claim 3 wherein said first fibers comprise an inelastic crystalline propylene polymer and further wherein the amorphous polyolefin polymer of said second fibers comprises a propylene elastomer and about 10% to about 50%, by weight, of the polymeric portion of said second fibers.
11. A durable sorbent comprising:
a first layer of thermoplastic polymer meltblown fibers having an average fiber size of less than about 8 micrometers;
a second layer autogenously bonded to said first layer, said second layer
5 comprising meltblown fibers having an average fiber size equal to or greater than the average fiber size of the first layer and further wherein the polymeric portion of said fibers of the second layer comprise a blend of from about 95% by weight to about 50% by weight of a crystalline polyolefin and from about 50% by weight to about 5% by weight of an amorphous polyolefin; and
10 wherein said sorbent has an abrasion resistance in excess of 500 cycles under the reciprocal abrasion test.
12. The sorbent of claim 11 wherein said first and second layers have a combined basis weight in excess of about 50 g/m² and an absorbent capacity in excess of about 8 grams.
13. The sorbent of claim 12 wherein the basis weight ratio of the first layer to the second layer is between about 2:1 and about 15:1.
14. The sorbent of claim 13 wherein the fibers of said first layer comprise propylene polymer.

15. The sorbent of claim 14 wherein said first layer comprises a crystalline propylene polymer and further wherein the crystalline polyolefin of said second layer comprises a crystalline propylene polymer.
16. The sorbent of claim 15 wherein said amorphous polyolefin polymer of said second layer is selected from the group consisting of propylene homopolymers, ethylene-propylene polymers, propylene-butene polymers and propylene-alphaolefins polymers.
17. The sorbent of claim 16 wherein said amorphous polyolefin of said second layer comprises a polymer having less than 10% crystallinity.
18. The sorbent of claim 15 wherein the fibers of said first layer comprise an inelastic crystalline propylene polymer and wherein the amorphous polyolefin polymer of said second layer comprises a propylene elastomer.
19. The sorbent of claim 15 wherein said amorphous polyolefin polymer of said second layer comprises between about 5% and about 35%, by weight, of the polymeric portion of said fibers.
20. The sorbent material of claim 11 wherein the fibers of said first layer comprise an inelastic crystalline propylene polymer and further wherein the fibers of said second layer have an average fiber size in excess of 15 micrometers and comprise a blend of an inelastic crystalline propylene polymer and an amorphous propylene polymer and further wherein said sorbent material has an abrasion resistance in excess of about 1000 cycles under the reciprocal abrasion test and further wherein said second layer has a basis weight less than about 68 g/m².
21. A durable multilayer nonwoven web composite material comprising:
a first layer of first meltblown fibers, said first meltblown fibers comprising a thermoplastic polymer and having an average fiber size of less than about 8 micrometers;
a second layer autogenously bonded to said first layer and comprising an outermost
5 layer of said multilayer nonwoven web composite material, said second layer comprising second meltblown fibers and wherein the polymeric portion of said second fibers comprises from 5% to 95% of an amorphous polyolefin and from 5% to 95% of a crystalline polyolefin; and

wherein said multilayer nonwoven web composite material contains a tertiary material selected from the group consisting of particulate materials and short fibrous matter, said tertiary material dispersed within at least one of said first and second layers.

22. The multilayer nonwoven web of claim 21 wherein the first fibers of said first layer comprise a propylene polymer.

23. The multilayer nonwoven web of claim 22 wherein said crystalline polyolefin of said second fibers comprises a crystalline propylene polymer and further wherein said amorphous polyolefin of said second fibers comprises between about 10% and about 50% by weight of the second fibers.

24. The multilayer nonwoven web of claim 23 wherein said amorphous polyolefin of said second layer comprises an amorphous propylene polymer.

25. The multilayer nonwoven web of claim 23 wherein said amorphous polyolefin polymer of said second layer comprises a propylene elastomer.

26. The multilayer nonwoven web of claim 25 wherein the second layer has a basis weight less than about 34 g/m² and said first layer has a basis weight equal to or greater than the basis weight of the second layer and further wherein said multilayer laminate has an abrasion resistance of at least about 250 cycles.

27. The multilayer nonwoven web of claim 23 wherein the secondary material is selected from the group consisting of pulp and cellulosic fibers.

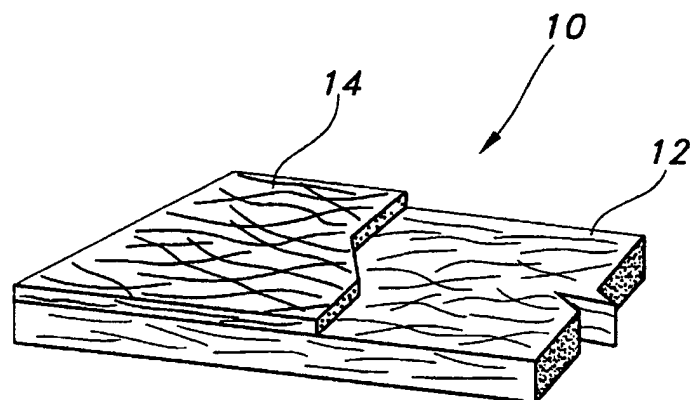
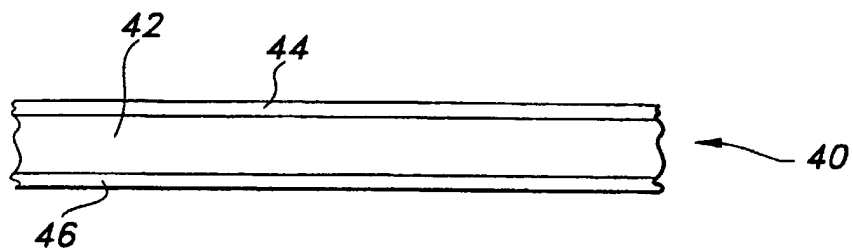
28. The multilayer nonwoven web of claim 27 wherein said first fibers comprise an inelastic crystalline propylene polymer and further wherein said crystalline polyolefin of said second fibers comprises an inelastic crystalline propylene polymer.

29. The multilayer nonwoven web of claim 25 further comprising a third layer of meltblown fibers autogenously bonded to said first layer and wherein the polymeric portion of said fibers comprising the third layer comprises from about 10% to 50% of an amorphous polyolefin and from 90% to 50% of a crystalline propylene polymer.

30. The multilayer nonwoven web of claim 29 wherein said secondary material comprises pulp and further wherein said pulp is dispersed within each of said first, second and third layers.

31. The multilayer nonwoven web of claim 30 wherein said multilayer nonwoven web has a basis weight less than about 80 g/m^2 and further wherein the basis weight of said first layer is at least twice that of said second layer and further wherein the basis weight of said first layer is at least twice that of said third layer.

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**FIG 1****FIG 3**

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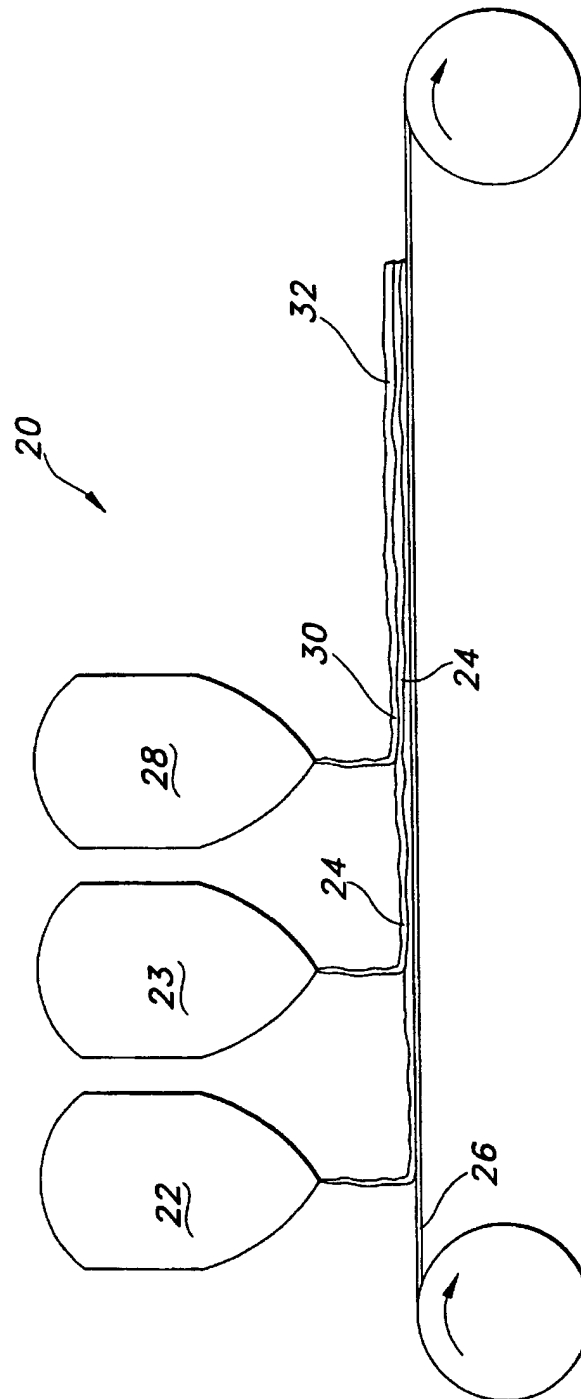
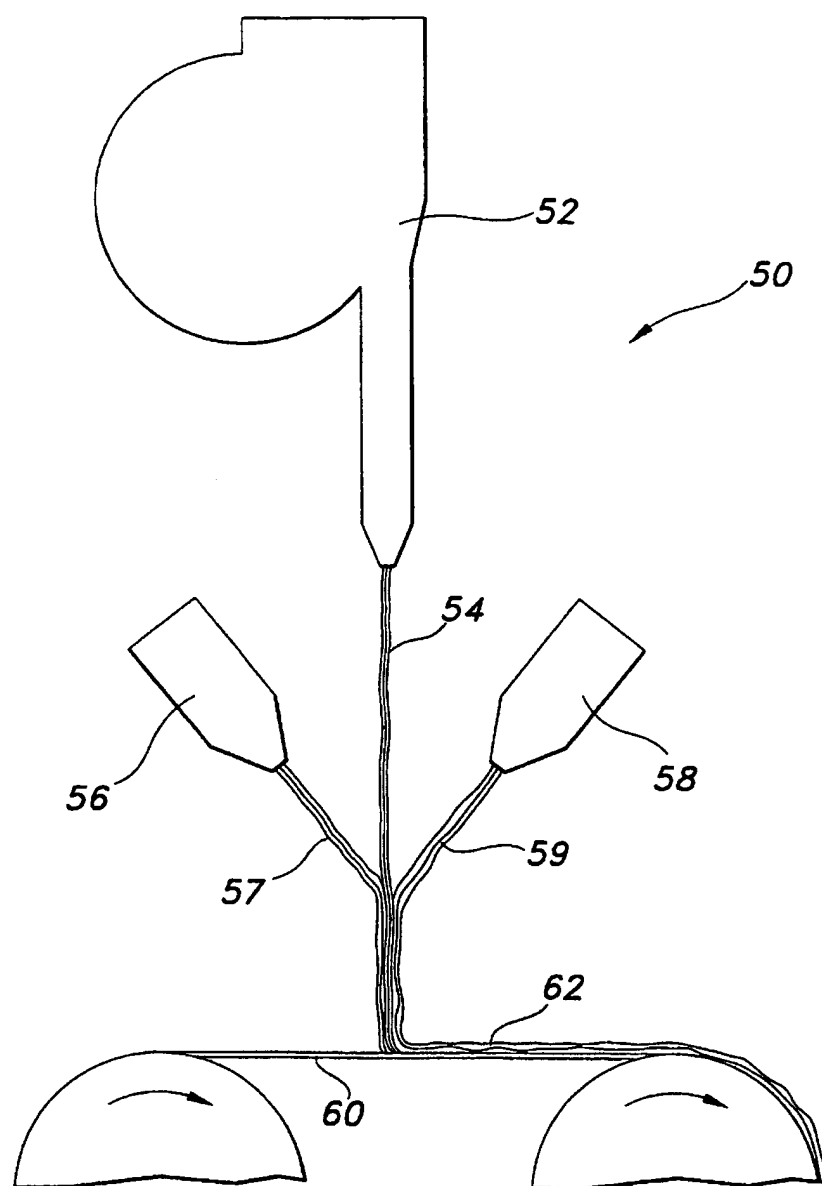


FIG 2

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**FIG 4**

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/18000

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D04H13/00 D01F6/46 B32B5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D04H D01F C08L B32B A47L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 37723 A (KIMBERLY CLARK CO) 29 June 2000 (2000-06-29) the whole document	1,5,11, 21,22
A	US 5 811 178 A (LAU JARK CHONG ET AL) 22 September 1998 (1998-09-22) cited in the application the whole document	1-31
A	US 5 639 541 A (ADAM GABRIEL HAMMAN) 17 June 1997 (1997-06-17) cited in the application the whole document	1-31
A	US 4 659 609 A (LAMERS GREGORY C ET AL) 21 April 1987 (1987-04-21) cited in the application the whole document	1-31
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *&* document member of the same patent family

Date of the actual completion of the international search

15 November 2000

Date of mailing of the international search report

30/11/2000

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INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 00/18000

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 590 307 A (KIMBERLY CLARK CO) 6 April 1994 (1994-04-06) cited in the application the whole document ---	1-31
A	WO 97 34037 A (KIMBERLY CLARK CO) 18 September 1997 (1997-09-18) page 18, paragraph 3 -column 21, paragraph 2 ---	1-31
A	US 5 460 884 A (KOBYLIVKER PETER M ET AL) 24 October 1995 (1995-10-24) the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/18000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0037723 A	29-06-2000	AU 2711900 A	12-07-2000
US 5811178 A	22-09-1998	US 5652048 A	29-07-1997
		US 5711970 A	27-01-1998
		AU 698075 B	22-10-1998
		AU 6648896 A	26-02-1997
		BR 9610447 A	08-06-1999
		CA 2224906 A	13-02-1997
		CN 1198193 A	04-11-1998
		EP 0842310 A	20-05-1998
		WO 9705306 A	13-02-1997
US 5639541 A	17-06-1997	AU 1411097 A	17-07-1997
		CA 2238441 A	03-07-1997
		WO 9723678 A	03-07-1997
US 4659609 A	21-04-1987	CA 1316693 A	27-04-1993
		EP 0244934 A	11-11-1987
		JP 63028570 A	06-02-1988
EP 0590307 A	06-04-1994	US 5350624 A	27-09-1994
		AU 672229 B	26-09-1996
		AU 4877593 A	21-04-1994
		CA 2089805 A	06-04-1994
		CN 1087392 A, B	01-06-1994
		DE 69322572 D	28-01-1999
		DE 69322572 T	29-04-1999
		EG 20242 A	31-05-1998
		JP 6257055 A	13-09-1994
		KR 236748 B	02-03-2000
		MX 9306128 A	29-04-1994
		US 5508102 A	16-04-1996
		ZA 9305967 A	15-03-1994
WO 9734037 A	18-09-1997	US 6103647 A	15-08-2000
		AU 705599 B	27-05-1999
		AU 2128897 A	01-10-1997
		BR 9707985 A	27-07-1999
		CA 2247169 A	18-09-1997
		CN 1217759 A	26-05-1999
		EP 0886690 A	30-12-1998
US 5460884 A	24-10-1995	AU 687599 B	26-02-1998
		AU 3151295 A	14-03-1996
		BR 9508623 A	18-11-1997
		CA 2154496 A	26-02-1996
		DE 69508771 D	06-05-1999
		DE 69508771 T	02-12-1999
		EP 0777770 A	11-06-1997
		ES 2129212 T	01-06-1999
		PL 318763 A	07-07-1997
		WO 9606210 A	29-02-1996
		US 5607798 A	04-03-1997

